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請求の範囲

1. 少なくとも一つの還元性金属化合物と少なくとも一つの還元剤の混合物を機械的活性化に付し、金属又は合金を生成させ、

所望により合金又は非合金を供給する化合物を反応混合物中に含有させてセラミック材料生成物を生成させ、そして/又は

所望により少なくとも一つの他の金属又はメタロイドを、セラミック材料又は合金生成物に取り込むために反応混合物に含有させることを特徴とする、金属、合金又はセラミック材料の生成法。

2. 少なくとも一つの還元剤の存在下、還元性金属化合物を機械的活性化に付し、金属生成物を生成させることを特徴とする、請求項1の方法。

3. 金属類混合物又は合金生成物を生成させるのに用いられる少なくとも一つの還元剤の存在下、二又はそれ以上の還元性金属化合物を機械的活性化に付すことを特徴とする、請求項1の方法。

4. さらに別の金属及び/又はメタロイドを反応混合物に含有させてさらに別の金属又はメタロイドを金属類混合物又は合金生成物中

に取り込むことを特徴とする、請求項2又は請求項3の方法。

5. 少なくとも一つの還元剤及び非金属又は非金属を供給する化合物の存在下、少なくとも一つの還元性金属化合物を機械的活性化に付し、セラミック材料生成物を生成させることを特徴とする、請求項1の方法。

6. さらに別の金属及び/又はメタロイドを反応混合物に含有させて、さらに別の金属及び/又はメタロイドをセラミック材料生成物に取り込むことを特徴とする、請求項3の方法。

7. 反応混合物を高エネルギーボールミル装置により機械的に活性化することを特徴とする、先行請求項のいずれか一つの方法。

8. 機械的活性化を不活性又は還元雰囲気下に行なうことを特徴とする、先行請求項のいずれか一つの方法。

9. 潤滑剤を反応混合物に添加することを特徴とする、先行請求項のいずれか一つの方法。

10. 機械的活性化を間欠的に実施することを特徴とする、先行請求項のいずれか一つの方法。

11. 還元性金属化合物が金属硫化物類、硫化物類、ハロゲン化合物類、水素化合物類、置換物類、炭化物類及び／又はリン酸塩類から選択されることを特徴とする、先行請求項のいずれか一つの方法。

12. 還元剤がカルシウム、マグネシウム及びナトリウムから選択されることを特徴とする、先行請求項のいずれか一つの方法。

13. 還元剤が炭化水素に溶解したアルキルリチウム、液体アンモニアに溶解したアルカリ金属及びナトリウム-カリウム合金から選択される状態であることを特徴とする、請求項1ないし10のいずれか一つの方法。

14. 還元剤が水素、塩素及び一酸化炭素から選択される気体であることを特徴とする、請求項1ないし11のいずれか一つの方法。

15. 方法により生成される金属、合金又はセラミック材料が超微粒状態を有することを特徴とする、先行請求項のいずれか一つの方法。

16. セラミック材料生成物がセラミック化合物、炭化物、窒

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化物又は炭化物であることを特徴とする、請求項1又は5ないし1

6のいずれか一つの方法。

17. セラミック材料生成物が超電導体であることを特徴とする、請求項1又は6ないし16のいずれか一つの方法。

明 細 書

金属類、合金類及びセラミック材料類の製造法

本発明は、金属類、合金類及びセラミック材料類の製造法に関する。より詳しくは、本発明は、還元性金属化合物(類)を機械的活性化、化学還元に対し、金属類、合金類又はセラミック材料類を生成することに関する。

大部分の金属元素類は、天然では、鉱石水溶液中、炭化物類、硫化物類又はリン酸塩類として存在する。精製工程は、一般に鉱石から純粋炭化物類、硫化物類及び／又はリン酸塩類を分離並びに炭化物、硫化物及び／又はリン酸塩を純金属に変換する一又はそれ以上の還元工程を含む。

一方、還元工程は、精製されている個々の元素に特異的であるが、通常、炭化物、硫化物及び／又はリン酸塩が前記のより正の電位をもちた元素により還元される化学反応又は電位により駆動される電気化学反応のいずれかを含む。化学還元方法は、しばしば、気相又は液相中で行なわれる一又はそれ以上の反応を伴う高温を必要とし、

これにより、異なる高反応速度に達することができる。

ほとんどの慣用方法で、純金属類が生成し、これらは次いで他の金属類と混合し、種々の溶解及び冶金技術を用いて合金類を形成する。ある場合には純金属類から合金類を製造することは技術的に困難であるかコストがかかり、金属硫化物類の適当な混合物から出発する化学還元方法を計画することが考えられる。硫化物の混合物は、適当な還元剤の添加及び高温により、一歩階で所望の合金組成物に直接還元する。このような方法で、希土類元素群の製造に用いられる還元抽出工程及び共還元 (co-reduction) 工程を含む。これらの工程は還元剤としてカルシウムを使用し、1000℃以上の温度に加熱することを含む。

それらの純粋組成成分を溶解することによる合金類の製造の別な方法は、機械的合金化方法として知られている。機械的合金化法は、溶解又は高温を必要とすることなく、純粋組成成分の粉末から合金類の製造を可能にする。機械的合金化方法は、高エネルギーボールミル中で実施しうる。ミル粉砕操作により、ボール-粉砕ボール-

ル及びボール-粉末-容器衝突の際に粉末粒子の粉碎と冷間接合が繰り返して生ずる。合金化方法は、冷間接合により結合した粒子的に滑潤な表面を交互する相互拡散反応として起まる。充分な時間を与えることにより、機械的合金化方法は原子レベルで真の合金を製造できる。使用手段により調整することは、きもなければ不可能であった機械的合金化方法により残りの合金類を調整することが可能であることを示す。又、機械的合金化は、特に元素粉末が反応の大量の陽極、並びに金属間化合物類及び分散合金類を示す場合、アモルファス合金類を製造するのに用いることができる。

本発明は、還元性金属化合物(類)から金属類又は合金類を製造するのに適した「機械的活性化、化学還元」と称する新規な化学還元方法に関する。機械的活性化、化学還元方法は、本質的に、機械的合金化方法の適用である。機械的活性化、化学還元の間、化学還元が機械的作用の結晶として起こり、金属化合物(類)を金属又は合金に還元することになる。

本発明の機械的活性化、化学還元方法は、又、セラミック材料類、

混合物又は合金生成物を生成するのに用いる。

特に又は付加的に他の金属及び/又はメタロイドを反応混合物中に含有してもよく、これにより、この他の金属及び/又はメタロイドを金属、金属混合物又は合金生成物中に取り込ませうる。

さらに他の態様では、非金属又は非金属を供給する化合物を反応混合物に含有させて、セラミック材料を生成しうる。

ここでは又、他の金属及び/又はメタロイドを反応混合物中に含有させ、この他の金属及び/又はメタロイドをセラミック材料生成物中に取り込ませうる。特に好ましい態様においては、機械的活性化は、高エネルギーボールミル粉碎により行なう。用語「高エネルギーミル粉碎」とは、ボール成分の相当部分が連続的に且つ断片的に恒対運動の状態で維持し、そして、ボールに付着されたエネルギーが、ボール-粉末-ボール及びボール-粉末-容器衝突の際の粉末粒子の粉碎と接合を起こすのに充分であるように、充分な機械的エネルギーが全投入量に適用される場合にボールミルに生ずる状態をいう。

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即ち、金属類及び非金属類の化合物類である一又はそれ以上の物を含む材料類の製造に及ぶ。即ち、方法は、鉄金属類及び他の金属類又はメタロイド類を含むそれらの合金類から金属類及び/又はメタロイド類をそれらの組成物中に含みうるセラミック材料類に及ぶ生成物を製造することができる。

本発明によれば、少なくとも還元性金属化合物と少なくとも一つの還元剤の混合物を機械的活性化に付し、金属又は合金を生成させる。

所望により非金属又は非金属を供給する化合物を反応混合物中に含有させてセラミック材料生成物を生成させ、そして/又は、

所望により少なくとも一つの他の金属又はメタロイドを、セラミック材料又は合金生成物に取り込むために反応混合物に含有させることも特徴とする金属、合金又はセラミック材料の製造法を提供する。即ち、方法の一態様では、少なくとも一つの還元剤の存在下、還元性金属化合物を機械的活性化に付し、金属生成物を生成させる。

別の態様では、二又はそれ以上の還元性金属化合物類を金属類の

高エネルギーボールミル内で、固体粒子、例えば金属化合物(類)、非金属(類)又は非金属(類)を提供する化合物(類)、及び還元剤粒子は、繰り返し整形し、粉碎し、そして混合する。粒子が衝突するボール間にはまると、衝突力が粒子を歪形し、粉碎し、原子的に滑潤な新しい表面を生ずる。滑潤な表面が接触すると、それらは互いに接合する。このような表面は容易に酸化されるので、ミル粉碎操作は、好ましくは不活性又は還元雰囲気で行なう。

高エネルギーボールミルは、全ての適当な周知の型のものであってもよい。例えば、ミルは、円筒に羽根車の系列を備えた垂直ドラムを含みうる。強力なモーターが羽根車を回転させ、羽根車は駆動ドラム間で鉄のボールを撚拌する。このような機構は、典型的な慣用ミルよりも10倍以上の撚拌速度に達することができる。「アトライター (attritor)」として一般に知られているこの型のミルは、米国特許第2,741,848号及びベリズ・ケミカル・エンジニアーズ・ハンドブック、5版、1973、p.29からp.30頁に記載されている。別に、高エネルギーボールミルは重力依存型ボ

ールミル、例えば米国特許第4,627,959号記載のものであり
らる。

機械的活性化は高エネルギーボールミル以外の手段によって達し
ることが認識されるであろう。本明細書では、用語「機械的活
性化」は、機械的手段によって粉末粒子の形状、集合及び粉砕を起
こす全ての方法を含む。即ち、方法、例えば治漏圧延又は押出加工
を含む。

以下の記載において、本発明の好ましい特徴及び特色に関する選
好のために、高エネルギーボールミル粉砕による機械的活性化を引
用する。しかしながら、本発明はこの技術に限定されないこと又、同
様の効果を行う他の機械的活性化方法がボールミル粉砕に代わる
ことができることが認識される。

還元剤は固体、液体又は気体でありうる。又、二又はそれ以上の
還元剤を要すれば用いる。固体還元剤により、還元工程は、金属
化合物(顆)の圧縮及び集合の間に接触又はその近くで起こる。この
工程は、金属、合金又はセラミック材料が形成するまで続く。

10:1ないし30:1

ミル粉砕時間 72時間以下、より好ましくは24時間
以下

雰囲気 気体气氛又は不活性ガス、例えばアルゴン
又は純窒素及び水含量が100ppm以下
000部以下の窒素

潤滑剤 全ての不活性液体、例えば加水ナトリウム

高エネルギーボールミル粉砕の間、ミルの温度は衝突工程によ
り発生する熱により上昇する。加えて、機械的還元反応の発熱効果
が過度に付加の上昇を起こしうる。ある場合には、反応速度が充分
に高く、そのため、摩擦成分の自己加熱が結果として生じ、粉末の
融解が起こりうる。この自己加熱工程は、「自己伝播高温合成」(e
self-propagating high temperature synthesis)として知られてい
る。自己加熱の間に形成する生成物は、鉄くみル粉砕により容易に
還元される。

燃料に要するミル粉砕時間は、ミル粉砕の最初の期間後ミルを停

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液体又は気体還元剤により、反応は、高エネルギーボールミル中、
ボール/粉末衝突により生じた新鮮な金属化合物表面と還元雰囲気
との接触の結果として起きる。方法の効率、還元されている金属
化合物(顆)と用いられる加工パラメーターに依存する。後者は衝突
エネルギー、衝突周波数、ボール/粉末質量比、ボール質量、ボー
ルの数、ミル粉砕時間、温度、雰囲気及び潤滑剤を含む。潤滑剤又
は他の方法潤滑剤の添加は、金属化合物顆が還元される環境を強化
しうる。潤滑剤又は他の方法潤滑剤は、粉砕及び集合の速度を調節
し、摩擦を防止する熱源制御として作用しうる。

加工パラメーターは、処理される材料の性質及び用いた機械的
活性化に依存する。実施例の方法により、以下の高エネルギーボー
ルミル粉砕に適したパラメーターが好ましい。

衝突エネルギー 0.1-1.0J、より好ましくは約0.2
5J

衝突周波数 1-200Hz

ボール/粉末質量比 2:1ないし40:1、より好ましくは

止すること、時間の固定期間に適した粉末不動(powder stationary
ity)を保持すること、次いでミル粉砕工程を促すことにより本質的
に短くしうる。この期間は、又、連続的ミル粉砕の間に提供がない
これらの反応に摩擦を起こすのに用いうる。

本発明の好適は、又、機械的活性化の結果として、超微粒粒子
の金属、合金又はセラミック材料顆を直接生成するのに用いる。
これらの超微粒粒子は、1ミクロン又はそれ以下の粒度を有しうる。

方法は、酸化物類、硫化物類、ハロゲン化合物類、水素化合物類、窒
化物類、炭化物類及び/又はリン酸塩類を含む広範囲の金属化合物
顆の還元に適応できる。唯一の制約は、還元工程に伴う熱電気自由
エネルギー変化が許容することである。固体反応材料顆の粒子は、
新鮮な表面を還元剤にさらすために機械的活性化の間、露出される
ことが必要である。露出は又、系内で生じる化学反応の結果として
も生じうる。

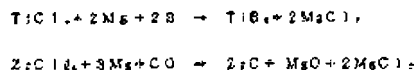
上記のように、還元剤は固体、液体又は気体でありうる。炭素固

体還元剤は、高い電気的陰性固体、例えばカルシウム、マグネシウム及びナトリウムを含む。適当な溶媒還元剤は、炭化水素類に溶解したアルキルリチウム類、液体アンモニアに溶解したアルカリ金属類及びナトリウム-カリウム合金類を含む。気体還元剤の例は、水素、塩素及び一酸化炭素を含む。

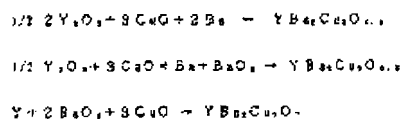
機械的活性化の適成のため、還元剤は標準的化学手段により反応生成物から除去されうる。例えば、カルシウム金属を還元剤として用いると、得られる酸化カルシウムは、水との反応により水合されうる。次いで得られる水酸化カルシウムを適当な溶媒に溶解し、溶媒により除去しうる。ある場合には、方法の達成のために還元成分を除去しなくてもよい。例えば反応の間に形成する酸化物粒子は、次いで分散硬化合金中、硬質相(hard phase)の基盤を形成しうる。

以上の記載から、本発明が特定の金属化合物又は還元剤類の使用に限定されないことは明らかであらう。さらに、還元される材料又は還元剤(類)は、材料類の少くとも一つが固相であれば、固体、液体又は気体のいずれでもよい。

での工業技術材料類又は生成物類(又はそれらの一部)を含む。本発明の方法により生成されうるセラミック材料類のタイプは、セラミック化合物類、炭化物類、窒化物類及び無機物類を含む。例えばチタニウム、及び炭化ジルコニウムは以下の反応により生成しうる。



本発明の方法は、又、セラミック材料超伝導体類、例えば以下の反応に示されるものを生成するのに用いる。



上記反応の一つの利点は、超伝導体の酸素含量が、熱処理によるよりも化学量論により固定していることである。

上記した機械的活性化化学還元方法は、慣習的工よりも数多くの利点を有する。

特表平4-502480 (B)

本明細書で使用される用語「合金」は、二又はそれ以上の金属類及び/又はメタロイド類の密接な組合せから形成される金属固体を意味する。本発明により生成されうる合金類は、必要成分が遷移金属グループ又はランタニド系列(希土類元素類)からであるものを含む。さらに全ての二成分、三成分及びより高い成分の合金類を含む。より少ない付加物類は、メタロイド類又は非金属類、例えばホウ素又は炭素、例えば、希土類元素永久磁石材料類の製造に、例えばNd、Fe、Coを含む。

合金類は、未知固溶体類、化学量論的化合物類でありうるか又は、各相が固溶体又は化学量論的化合物類でありうる二又はそれ以上の相より成りうる。本方法により生成されうる金属類及び/又は合金類の例は、珪、鋁、亜鉛、鉄、チタニウム、アルファ又はベータ黄銅(銅Zn)、NiTi、SiC、及びミッシュメタルを含む。

本明細書で使用される用語「セラミック材料」は、金属類及び非金属類の化合物類である一又はそれ以上の相を含む材料をいう。セラミック材料類は、金属類及び合金類以外の化学的に異質である、金

1. 方法は、還元金属化合物類から、高温圧を用いることなく同時に密接な金属類を直接形成させる。
2. 方法は、還元性化合物類から、化合物類を純粋金属類にまで加工し、次いで合金類を形成するために純粋金属類を混合することなく、粉末生成物を直接形成させる。
3. 方法は、バルク金属、合金又はセラミック材料をまず製造し、次いでそれを粉末形に変えることなく、粉末生成物を直接形成させる。
4. 方法は、金属、合金又はセラミック材料をまず生成し、次いで超微粒微粒子を生成させることなく、金属類、合金類又はセラミック材料の超微粒微粒子を直接形成させる。

利点(1)ないし(4)は、慣習的高温(溶解/粉末又は粉末冶金)を用いて生成することが困難である反応塩元素類及び合金、例えば希土類元素の場合に重要である。得られる生成物は、広範囲の粉末冶金への応用に適している。

本発明を以下の実施例により記述し、示す。これらの実施例は、

いずれにせよ本発明を限定するものと解釈すべきでない。

実施例1

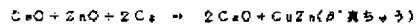
酸化銅及びカルシウムを、S P C X マデル B D Q O とキリーノミ、投入ねじパイアル及び3つの酸化タンゲステンボールを用いた窒素雰囲気(N₂ガス)中、潤滑剤としてトルエンを用いミル粉砕した。ボールの全質量は約24グラムでボール対粉末質量比は約8:1であった。さらに10%のカルシウムを加えた等原子質量の銅(酸化銅として)及びカルシウムを24時間ミル粉砕した。約82のトルエンを潤滑剤として用いた。ミル粉砕ののち、反応生成物をX線回折により同定した。ミル粉砕は反応:



を生じ、時間の関数として次第に起きていることが判った。20時間ミル粉砕後、反応は完了した。ミル粉砕完了後、酸化カルシウムと炭素カルシウムを、水との反応によりCaOを中和することを含む標準的技術を用いて除去した。炭素で得られるCa(OH)₂を希硫酸に溶解し、濾過により除去した。

実施例4

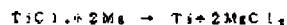
等原子質量のZn(ZnOとして)及びCa(CuOとして)を実施例2及び8のそれぞれ10%過剰のカルシウムと共に乾燥ミル粉砕した。この実験では、鋼パイアルを70℃に冷却し、アルゴンガスを不活性雰囲気として用いた。ミル粉砕時間は24時間であった。ミル粉砕の完了において、生成物は2¹ CuZn合金酸化銅及びCaOからなる。前述反応は



である。

実施例5

等原子質量のチタニウム(液体四塩化チタニウムとして)及びマグネシウムを、付加約15%マグネシウムと共に、全質量80グラムの8つのステンレススチールボールを用い実施例1のようにミル粉砕した。ミル粉砕は反応:



を生じ時間の関数として次第に起きた。18時間のミル粉砕後、炭

実施例2

酸化銅とカルシウムを、ミル粉砕前に潤滑剤を粉末に添加せず、又、鋼ボールを酸化タンゲステンに置き換えた以外は実施例1に記載したようにしてミル粉砕した。粉末を24時間まで種々の時間で「乾燥」ミル粉砕した。約10分のミル粉砕後、自然発生の燃焼及び粉末の溶解を起こすのに充分な熱が、還元工程の反応の開始により発生した。燃焼工程の生成物の実験により、Cu、CuO、Ca、CaO、CaCO₃、Cu₂O及びCu₂CaOの存在を示した。さらに24時間のミル粉砕後、燃焼的還元と自酸化が起きて、極値する最終値はCaO及びCuであった。

実施例3

酸化銅及びニッケルを実施例2のようにミル粉砕した。ミル粉砕は還元反応:



を生じ、24時間のミル粉砕後、反応が完了するように次第に起きた。実施例2におけるような自己燃焼の数は見られなかった。

反応が完了した。ミル粉砕の完了において、以下の手段の一つを用いてMgCl₂及び炭素反応MgをTiから除去した。

手段1、ミル粉砕粉末を水中10%HClの溶液で洗浄しMgCl₂及びMgを溶解し、炭素で蒸留水で洗浄し濾過した。手段2により、MgCl₂及びMgを、10⁻⁴トールの真空下、900℃で24時間真空炉管により除去した。手段1及び2の結果、それぞれ、約0.2及び2.5μmの平均粉末サイズとなった。

実施例6

四塩化チタニウム及びマグネシウムを、ミル粉砕をパイアルを冷却することにより-75℃の温度で実施したこと以外実施例5に記載したようにミル粉砕した。-75℃で、四塩化チタニウムは固体(融点=-24℃)で、ミル粉砕は固相反応を伴った。3時間のミル粉砕後、反応は完了した。

実施例7

合金Ti-6%V-4%Alを形成するのに適した量のTiCl₄、VCl₃及びAl₂Cl₃を15%過剰マグネシウムと共にミル粉砕した。

特表平4-502430 (7)

ミル粉砕は、実施例5に記載したように実施し、合金粉末が18時間後に形成した。

実施例8

導電性質量の面密(2.0として)及びチタニウムを、10%過剰のチタニウムとともに実施例1に記載したように乾燥ミル粉砕した。
X線回折分析は、反応:



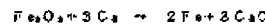
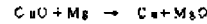
が約5時間後開始し、48時間後には本質的に完了したことを示した。乾燥反応は起きなかった。

別の系の試験で、試料を6.5時間ミル粉砕した。ミル粉砕は、2及び13時間の間の時間の一定期間停止した。13時間保持した試料では、乾燥は、ミル粉砕を再開直後2秒に起きた。乾燥に要する時間は保持時間の減少と共に増加し、6時間保持した試料については、乾燥はミル粉砕を再開直後7.5秒で起きた。乾燥は2時間停止を要した試料では見られなかった。13時間保持後の乾燥に要する時間は、乾燥ミル粉砕時間の増加と共に減少することが有り、6

時間ミル粉砕した試料では乾燥は1秒後に起こり、5時間後では乾燥は8秒後に起こり、一方、4.5時間ミル粉砕した試料では乾燥は起きなかった。

実施例9

以下の反応は、実施例1におけるように、表示の反応物質をミル粉砕することにより実施した。10%の化学量論的過剰の還元剤を含む約8グラムの粉末を全試験で用いた。ミル粉砕時間は数秒ないし48時間に渡った。



実施例10

全体組成 $Y_{0.8}Cu_{0.2}O_{1.8}$ を与えるのに適した質量の Y_2O_3 、 BaO 及び CaO を実施例2に記載されるようにミル粉砕した。約15分のミル粉砕後、反応:



が乾燥反応により起きた。

実施例11

全体組成 $Y_{0.8}Cu_{0.2}O_{1.8}$ を与えるのに適した質量の Y 、 BaO 、及び CaO を実施例2に記載されるようにミル粉砕した。約14分のミル粉砕後、反応:



が乾燥反応により起きた。

国際調査報告

International Application No. PCT/JP 88/00550		
1. CLASSIFICATION OF SUBJECT MATTER		
According to International Patent Classification (IPC) Class. H01B 1/00, H01B 1/02, H01B 1/04, H01B 1/06, H01B 1/08, H01B 1/10, H01B 1/12, H01B 1/14, H01B 1/16, H01B 1/18, H01B 1/20, H01B 1/22, H01B 1/24, H01B 1/26, H01B 1/28, H01B 1/30, H01B 1/32, H01B 1/34, H01B 1/36, H01B 1/38, H01B 1/40, H01B 1/42, H01B 1/44, H01B 1/46, H01B 1/48, H01B 1/50, H01B 1/52, H01B 1/54, H01B 1/56, H01B 1/58, H01B 1/60, H01B 1/62, H01B 1/64, H01B 1/66, H01B 1/68, H01B 1/70, H01B 1/72, H01B 1/74, H01B 1/76, H01B 1/78, H01B 1/80, H01B 1/82, H01B 1/84, H01B 1/86, H01B 1/88, H01B 1/90, H01B 1/92, H01B 1/94, H01B 1/96, H01B 1/98, H01B 2/00, H01B 2/02, H01B 2/04, H01B 2/06, H01B 2/08, H01B 2/10, H01B 2/12, H01B 2/14, H01B 2/16, H01B 2/18, H01B 2/20, H01B 2/22, H01B 2/24, H01B 2/26, H01B 2/28, H01B 2/30, H01B 2/32, H01B 2/34, H01B 2/36, H01B 2/38, H01B 2/40, H01B 2/42, H01B 2/44, H01B 2/46, H01B 2/48, H01B 2/50, H01B 2/52, H01B 2/54, H01B 2/56, H01B 2/58, H01B 2/60, H01B 2/62, H01B 2/64, H01B 2/66, H01B 2/68, H01B 2/70, H01B 2/72, H01B 2/74, H01B 2/76, H01B 2/78, H01B 2/80, 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
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PROCESS FOR THE PRODUCTION OF METALS, ALLOYS AND CERAMIC MATERIALS**Publication number:** JP4502490 (T)**Publication date:** 1992-05-07**Inventor(s):****Applicant(s):****Classification:**

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Abstract of corresponding document: **WO 9007012 (A1)**

A process for the production of a metal, alloy or ceramic material which comprises subjecting a mixture of at least one reducible metal compound and at least one reducing agent to mechanical activation to produce a metal or alloy. A ceramic material may be produced by including a non-metal, or a compound which provides the non-metal, in the reaction mixture. At least one other metal or a metalloid may also be included in the reaction mixture for incorporation into the ceramic material or alloy.

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<p>(54) Title: PROCESS FOR THE PRODUCTION OF METALS, ALLOYS AND CERAMIC MATERIALS</p> <p>(57) Abstract</p> <p>A process for the production of a metal, alloy or ceramic material which comprises subjecting a mixture of at least one reducible metal compound and at least one reducing agent to mechanical activation to produce a metal or alloy. A ceramic material may be produced by including a non-metal, or a compound which provides the non-metal, in the reaction mixture. At least one other metal or a metalloid may also be included in the reaction mixture for incorporation into the ceramic material or alloy.</p>		

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**PROCESS FOR THE PRODUCTION OF METALS, ALLOYS
AND CERAMIC MATERIALS**

25 This invention relates to a process for the
production of metals, alloys and ceramic materials. More
specifically, the invention is concerned with the
mechanically activated chemical reduction of reducible
metal compound(s) to produce metals, alloys or ceramic
30 materials.

Most metallic elements occur in nature as oxides
sulphides or phosphates in ore bodies. The refining
process generally involves separation of pure oxides,
35 sulphides and/or phosphates from the ore, and one or more
reduction processes to convert the oxide, sulphide and/or
phosphate to pure metal.

While the reduction process is specific to the
40 particular element being refined, it usually involves
either a chemical reaction, where the oxide, sulphide
and/or phosphate is reduced by a second, more

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electro-positive element, or an electrochemical reaction driven by an electrical potential. Chemical reduction processes frequently require high temperatures, with one or more of the reactants being in the gas or liquid phase, 5 so that sufficiently high reaction rates can be achieved.

In most conventional processes, pure metals are produced which are then mixed with other metals to form alloys using various melting and casting techniques. In 10 some instances, where the production of alloys from pure metals is technically difficult or costly, it is possible to design chemical reduction processes which start with an appropriate mixture of metal oxides. The oxide mixture is directly reduced in a single step to the desired alloy 15 composition by the addition of an appropriate reducing agent and high temperatures. Such processes include the reduction diffusion process and the co-reduction process used in the production of rare earth magnets. These processes use calcium as the reducing agent and involve 20 heating to temperatures of above 1000°C.

An alternative process to the production of alloys by melting their pure constituents is known as mechanical alloying. Mechanical alloying enables the production of 25 alloys from powders of the pure constituents without the need for melting or high temperatures. The mechanical alloying process may be carried out in a high energy ball mill. The milling action causes repeated fracture and cold welding of the powder particles during 30 ball-powder-ball and ball-powder-container collisions. The alloying process takes place as an inter-diffusion reaction across atomically clean surfaces joined by cold welding. Given sufficient time, the mechanical alloying process can produce a true alloy at the atomic level. It

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has been shown that it is possible to prepare certain alloys by the mechanical alloying process which were otherwise impossible to prepare by conventional means. It has also been shown that mechanical alloying can be used
5 to produce amorphous alloys, particularly when the elemental powders exhibit a large positive heat of reaction, as well as intermetallic compounds and dispersion hardened alloys.

10 The present invention is concerned with a new chemical reduction process termed "mechanically activated chemical reduction" for manufacturing metals or alloys from reducible metal compound(s). The mechanically activated chemical reduction process is essentially an
15 adaption of the mechanical alloying process. During the mechanically activated chemical reduction, chemical reduction reactions are caused to occur, as a consequence of the mechanical action, which results in the reduction of the metal compound(s) to the metal or alloy.

20 The mechanically activated chemical reduction process of the present invention also extends to the production of ceramic materials, that is, materials which contain one or more phases that are compounds of metals
25 and non-metals. Thus, the process is capable of producing products which range from pure metals and their alloys with other metals or metalloids through to ceramic materials, which may also include metals and/or metalloids in their composition.

30 According to the present invention there is provided a process for the production of a metal, alloy or ceramic material, characterised in that:

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a mixture of at least one reducible metal compound and at least one reducing agent is subjected to mechanical activation to produce a metal or alloy product;

5

optionally a non-metal, or a compound which provides the non-metal, is included in the reaction mixture to produce a ceramic material product; and/or

10

optionally at least one other metal or a metalloid is included in the reaction mixture for incorporation into the ceramic material or alloy product.

15

Thus, in one aspect of the process, a reducible metal compound is subjected to mechanical activation in the presence of at least one reducing agent to produce a metal product.

20

In another aspect, two or more reducible metal compounds may be used to produce a mixture of metals or an alloy product.

Alternatively or additionally a further metal and/or
25 metalloid may be included in the reaction mixture so that the further metal and/or metalloid is incorporated into the metal, metal mixture or alloy product.

In a still further embodiment, a non-metal, or
30 compound which provides the non-metal, may be included in the reaction mixture to produce a ceramic material.

Here again, a further metal and/or metalloid may be included the reaction mixture so that the further metal

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and/or metalloid is incorporated into the ceramic material product.

In a particularly preferred embodiment, the
5 mechanical activation is produced by high energy ball
milling. The term "high energy milling" refers to a
condition which is developed in the ball mill when
sufficient mechanical energy is applied to the total
charge such that a substantial portion of the ball
10 elements are continuously and kinetically maintained in a
state of relative motion and that the energy imparted to
the balls is sufficient to cause fracture and welding of
powder particles during ball-powder-ball and
ball-powder-container collisions.

15

In the high energy ball mill, solid particles, such
as, the metal compound(s), non-metal(s) or the
compound(s) which provide the non-metal(s), and the
reducing agent particles are repeatedly deformed,
20 fractured and rewelded. When particles are trapped
between colliding balls, the force of the impact deforms
and fractures particles, creating atomically clean new
surfaces. When the clean surfaces come in contact, they
weld together. Since such surfaces readily oxidize, the
25 milling operation is preferably conducted in an inert or
reducing atmosphere.

The high energy ball mill may be of any suitable
known type. For example, the mill may comprise a vertical
30 drum with a series of impellers inside it. A powerful
motor rotates the impellers, which in turn agitate the
steel balls in the drum. Such a machine can achieve
grinding rates more than ten times higher than those
typical of a conventional mill. A mill of this type,

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commonly known as an "attritor", is described in U.S. Patent No. 2,764,359 and in Perry's Chemical Engineer's Handbook, 5th edition, 1973, at pages 8-29 to 8-30.

Alternatively, the high energy ball mill may be a gravity
5 dependent ball mill such as that described in U.S. Patent No. 4,627,959.

It will be appreciated that the mechanical activation may be achieved by means other than high energy
10 ball milling. In this specification, the term "mechanical activation" includes any process which causes deformation, welding and fracture of the powder particles by mechanical means, and thus includes processes such as, cold rolling or extrusion.

15

For convenience, in the following description, relating to preferred aspects and features of the invention, reference will be made to mechanical activation by high energy ball milling. It will be appreciated,
20 however, that the invention is not limited to this technique and that other mechanical activation processes having the same effects can be substituted for ball milling.

25 The reducing agent may be solid, liquid or gaseous, and two or more reducing agents may be used if required. With solid reducing agents the reduction reaction occurs at or near the interfaces during the compaction and welding of the metal compound(s) and the reducing agent
30 particles. This process continues until the metal, alloy or ceramic material is formed.

With liquid or gaseous reducing agents, the reaction occurs as a result of the contact of fresh metal compound

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surfaces created by the ball/powder collisions in the high energy ball mill with the reducing atmosphere. The efficiency of the process will depend on the nature of the metal compound(s) being reduced and the processing parameters used. The latter include collision energy, collision frequency, ball/powder mass ratio, ball mass, number of balls, milling time, temperature, atmosphere and lubricant. The addition of a lubricant or other process control agent may enhance the environment in which the metal compounds are reduced. The lubricant or other process control agent modifies the rates of fracture and welding and may act as a thermal diluent, preventing combustion.

The processing parameters depend on the nature of the materials treated and the mechanical activation employed. By way of example, the following parameters for high energy ball milling are preferred.

Collision energy: 0.1 - 1.0J, more preferably about 0.25J

Collision frequency: 1 - 200 Hz

Ball/powder mass ratio: 2:1 to 40:1, more preferably 10:1 to 30:1

Milling time: less than 72 hours, more preferably less than 24 hours

Atmosphere: gaseous hydrogen or an inert gas, for example, argon or nitrogen with residual oxygen and water contents less than 100 parts per million

Lubricant: any inert liquid, for example, anhydrous toluene

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During high energy ball milling, the temperature in the mill will rise due to the heat generated by the collision processes. In addition, the exothermic nature of the mechanical reduction reaction may cause an additional rise in temperature. In some cases, the reaction rate will be sufficiently high so that self-combustion of the constituents will result and melting of the powders may occur. This self-combustion process is known as "self-propagating high temperature synthesis". The products formed during the self-combustion may be further reduced by subsequent milling.

15 The milling time required for combustion may be substantially shortened by stopping the mill after an initial period of milling, keeping the powder stationary for a fixed period of time and then recommencing the milling process. This procedure may also be used to cause
20 combustion to occur in those reactions where there is no combustion during continuous milling.

 The process of the invention may also be used to produce ultra-fine grain size particles of metals, alloys
25 or ceramic materials directly as a consequence of the mechanical activation. These ultra-fine particles may have a grain size of 1 micron or less.

 The process is applicable to the reduction of a wide
30 range of metal compounds including oxides, sulphides, halides, hydrides, nitrides, carbides and/or phosphates. The only limitations are that there must be a negative free energy change associated with the reduction process. It is necessary that the particles of solid reaction

- 9 -

materials are fractured during the mechanical activation to expose fresh surfaces to the reducing agent. The fracturing may also occur as a result of the chemical reactions occurring in the system.

5

As described above, the reducing agent may be solid, liquid or gaseous. Candidate solid reducing agents include highly electronegative solids such as calcium, magnesium and sodium. Suitable liquid reducing agents
10 include lithium alkyls dissolved in hydrocarbons, alkali metals dissolved in liquid ammonia and sodium-potassium alloys. Examples of gaseous reducing agents include hydrogen, chlorine and carbon monoxide.

15 On completion of the mechanical activation, the reducing agent may be removed from the reaction product by standard chemical means. For example, where calcium metal is used as the reducing agent, the resulting calcium oxide may be hydrated by reacting it with water. The
20 resultant calcium hydroxide may then be dissolved in a suitable solvent and removed by filtration. In some instances, it may not be necessary to remove the reducing elements on completion of the process. For example, the oxide particles formed during the reaction may then form
25 the basis of the hard phase in a dispersion hardened alloy.

It will be appreciated from the above description that the invention is not limited to the use of any particular metal compounds or reducing agents.
30 Furthermore, the material being reduced or the reducing agent(s) may be either solid, liquid or gas with the proviso that at least one of the materials is solid.

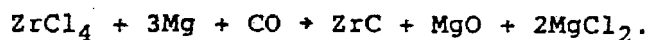
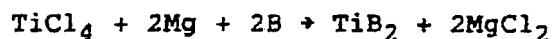
- 10 -

The term "alloy" as used herein refers to a metallic solid formed from an intimate combination of two or more metals and/or metalloids. The alloys which may be produced by the invention include those where the major element is from the transition metal group or the lanthanide series (the rare earths) and further include all binary, tertiary and higher order alloys. Minor additions may include metalloids or non-metals such as boron or carbon, for example, in the production of rare earth permanent magnet materials, such as, $\text{Nd}_{16}\text{Fe}_{26}\text{B}_8$.

The alloys may be single phase solid solutions, stoichiometric compounds or consist of two or more phases where each phase may be a solid solution or stoichiometric compound. Examples of the metals and/or alloys which may be produced by the process include copper, zinc, iron, titanium, alpha or beta brass (CuZn), NiTi , SmCo_5 and Misch metal.

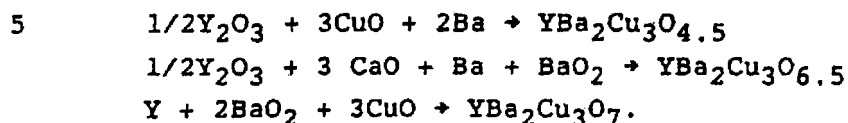
The term "ceramic material" as used herein refers to a material which contains one or more phases that are compounds of metals and non-metals. Ceramic materials comprise all engineering materials or products (or portions thereof) that are chemically inorganic, except metals and alloys. The types of ceramic materials that may be produced by the process of the invention include ceramic borides, carbides, nitrides and oxides. For example, titanium boride and zirconium carbide may be produced by the following reactions:

30



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The process of the invention may also be used to produce ceramic material superconductors, for example as shown in the following reactions:



One advantage of the above reactions is that the
10 oxygen content of the superconductor is fixed by the stoichiometry rather than by thermal treatment.

The mechanically activated chemical reduction process described above additionally possess a number of
15 advantages over conventional processing:

1. The process allows the direct formation of substantially pure metals from reducible metal compounds, without the use of high temperatures.
20
2. The process allows the direct formation of crystalline or amorphous alloys from reducible metal compounds without first having to process the compounds into pure metals and then combine the pure
25 metals to form the alloys.
3. The process allows the direct formation of powder products, without having to first manufacture the bulk metal, alloy or ceramic material and then
30 convert it to a powder form.
4. The process allows the direct formation of ultra-fine grain size particles of metals, alloys or ceramic material without having to first produce the

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metal, alloy or ceramic material and then generate ultra-fine grain size particles.

Advantages (1) to (4) are important in the case of reactive elements and alloys, such as the rare earths, which are difficult to produce using conventional high temperature (melt/cast or powder metallurgy) technologies. The resulting product should be suitable for a wide range of powder metallurgical applications.

10

The invention is further described in and illustrated by the following examples. These examples are not to be construed as limiting the invention in any way.

15 Example 1

Copper oxide and calcium were milled together using toluene as a lubricant in an inert atmosphere (N₂ gas) using a SPEX Model 8000 mixer/mill, hardened steel vial and 3 tungsten carbide balls. The total mass of the balls was approximately 24 grams and the ball to powder mass ratio was approximately 3:1. Equal atomic masses of copper (as copper oxide) and calcium, together with an additional 10% of calcium were milled for up to 24 hours. Approximately 6ml of toluene was used as the lubricant. Following milling the products of the reaction were identified by X-ray diffraction. The milling was found to cause the reaction:



to occur progressively as a function of time. After 24 hours milling the reaction was complete.

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At the completion of milling, the calcium oxide and the unreacted calcium were removed using a standard technique which involved hydrating the CaO by reacting 5 with water. The resulting Ca(OH)_2 was then dissolved in dilute mineral acid and removed by filtration.

Example 2

10 Copper oxide and calcium were milled together as detailed in Example 1, with the exception that no lubricant was added to the powders prior to milling and the steel balls were substituted for tungsten carbide. The powders were "dry" milled for various times up to 24 15 hours. After approximately 10 minutes of milling sufficient heat was generated by the exothermic heat of reaction of the reduction process, to cause spontaneous combustion and melting of the powders. Examination of the resulting products of the combustion process showed the 20 presence of Cu, CuO, Ca, CaO, CaCu_5 , Cu_2O and Cu_2CaO_3 . After milling for a further 24 hours, mechanical reduction and alloying occurred such that the final phases present were CaO and Cu.

25 Example 3

Copper oxide and nickel were milled together as in Example 2. Milling caused the reduction reaction:



to occur progressively such that after 24 hours milling the reaction was complete. No evidence of self-combustion as in Example 2 was observed.

Example 4

Equal atomic masses of Zn (as ZnO) and Cu (as CuO) were dry milled with 10% excess calcium as per Examples 2 and 3. In this experiment the steel vial was cooled to 0°C and argon gas was used as the inert atmosphere. The milling time was 24 hours. At the completion of milling, the products consisted of the β' CuZn intermetallic phase and CaO. The relevant reaction is:

Example 5

15

Equal atomic masses of titanium (as liquid titanium tetrachloride) and magnesium, together with an additional 15% magnesium were milled as in Example 1 using eight stainless steel balls of total mass 86 grams. The milling caused the reaction:



to occur progressively as a function of time. After 16 25 hours milling, the reaction was complete. At the completion of milling one of the following procedures was used to remove the MgCl_2 and unreacted Mg from the Ti.

In procedure 1, the milled powder was washed in a 30 solution of 10% HCl in water to dissolve the MgCl_2 and Mg, followed by washing in distilled water and filtration. With procedure 2, the MgCl_2 and Mg were removed by vacuum distillation for 24 hours at 900°C under a vacuum of 10^{-5} torr. Procedures 1 and 2 resulted in average powder sizes 35 of approximately 0.2 and 2 μm , respectively.

Example 6

Titanium tetrachloride and magnesium were milled together as described in Example 5, except that the milling was carried out at a temperature of -55°C by cooling the vial. At -55°C titanium tetrachloride is a solid (m.p. = -24°C) and milling involved a solid state reaction. After 3 hours milling, the reaction was 10 complete.

Example 7

Appropriate amounts of TiCl_4 , VCl_3 and AlCl_3 to form 15 the alloy Ti-6%V-4%Al were milled with 15% excess magnesium. The milling was carried out as described in Example 5 with the alloy powder being formed after 18 hours.

20 Example 8

Equal atomic masses of zinc (as ZnO) and titanium, together with an excess 10% titanium were dry milled as described in Example 1. X-ray diffraction analysis showed 25 that the reaction:



had initiated after approximately 5 hours and was 30 essentially complete after 49 hours. A combustion reaction did not occur.

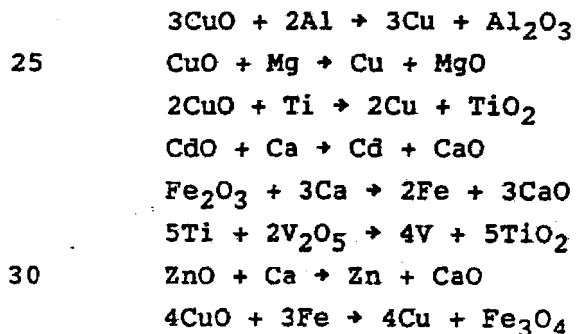
In a separate series of tests the samples were milled for 5.5 hours. The mill was turned off for periods

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of time between 2 and 13 hours. In the sample held for 13 hours, combustion occurred 2 seconds after milling was restarted. The time required for combustion increased with decreasing holding time, such that for a sample held 5 for 6 hours, combustion occurred 73 seconds after the mill was restarted. Combustion was not observed in a sample held stationary for 2 hours. The time required for combustion after holding for 13 hours was found to decrease with an increase in the initial milling time; 10 such that in a sample milled for 6 hours, combustion occurred after 1 second; after 5 hours, combustion occurred after 3 seconds while no combustion occurred in the sample milled for 4.5 hours.

15 Example 9

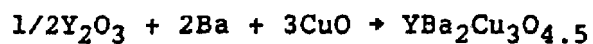
The following reactions were carried out by milling the indicated reactants together as in Example 1. Approximately 8 grams of powders were used in all tests, 20 including a 10% stoichiometric excess of the reducing agent. Milling times ranged from a few seconds to 48 hours.



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Example 10

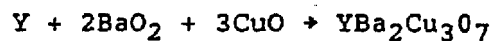
Appropriate masses of Y_2O_3 , Ba and CuO to give the overall composition $YBa_2Cu_3O_{4.5}$ were milled together as described in Example 2. After approximately 15 minutes of milling the reaction:



10 occurred by a combustion reaction.

Example 11

Appropriate masses of Y, BaO_2 and CuO to give the overall composition $YBa_2Cu_3O_7$ were milled together as described in Example 2. After approximately 14 minutes of milling the reaction:



20

occurred by a combustion reaction.

CLAIMS:

1. A process for the production of a metal, alloy or ceramic material, characterised in that:

5

a mixture of at least one reducible metal compound and at least one reducing agent is subjected to mechanical activation to produce a metal or alloy product;

10

optionally a non-metal, or a compound which provides the non-metal, is included in the reaction mixture to produce a ceramic material product; and/or

15

optionally at least one other metal or a metalloid is included in the reaction mixture for incorporation into the ceramic material or alloy product.

20

2. A process as claimed in Claim 1, characterised in that a reducible metal compound is subjected to mechanical activation in the presence of at least one reducing agent to produce a metal product.

25

3. A process as claimed in Claim 1, characterised in that two or more reducible metal compounds are subjected to mechanical activation in the presence of at least one reducing agent used to produce a mixture of metals or an alloy product.

30

4. A process as claimed in Claim 2 or Claim 3, characterised in that a further metal and/or a metalloid is included in the reaction mixture so that the further metal and/or metalloid is incorporated into the metal, metal mixture or alloy product.

35

5. A process as claimed in Claim 1, characterised in that at least one reducible metal compound is subjected to mechanical activation in the presence of at least one
5 reducing agent and a non-metal, or compound which provides the non-metal, to produce a ceramic material product.

6. A process as claimed in Claim 5, characterised in that a further metal and/or metalloid is included in the
10 reaction mixture so that the further metal and/or metalloid is incorporated into the ceramic material product.

7. A process as claimed in any one of the preceding
15 claims, characterised in that the reaction mixture is mechanically activated by high energy ball milling.

8. A process as claimed in any one of the preceding claims, characterised in that the mechanical activation is
20 conducted in an inert or reducing atmosphere.

9. A process as claimed in any one of the preceding claims, characterised in that a lubricant is added to the reaction mixture.
25

10. A process as claimed in any one of the preceding claims, characterised in that the mechanical activation is carried out intermittently.

30 11. A process as claimed in any one of the preceding claims, characterised in that the reducible metal compound is selected from metal oxides, sulphides, halides, hydrides, nitrides, carbides and/or phosphates.

12. A process as claimed in any one of the preceding claims, characterised in that the reducing agent is a solid selected from calcium, magnesium and sodium.

5 13. A process as claimed in any one of Claims 1 to 11 characterised in that the reducing agent is a liquid selected from lithium alkyls dissolved in hydrocarbons, alkali metals dissolved in liquid ammonia and a sodium-potassium alloy.

10

14. A process as claimed in any one of Claims 1 to 11 characterised in that the reducing agent is a gas selected from hydrogen, chlorine and carbon monoxide.

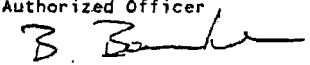
15 15. A process as claimed in any one of the preceding claims characterised in that the metal, alloy or ceramic material produced by the process has ultra-fine grain size particles.

20 16. A process as claimed in any one of Claims 1 or 5 to 15 characterised in that the ceramic material product is a ceramic boride, carbide, nitride or oxide.

17. A process as claimed in any one of Claims 1 or 5 to
25 16 characterised in that the ceramic material product is a superconductor.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 89/00550

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ⁴ C22B 5/00, 5/04, 5/12; C22C 1/04, 1/10; C04B 35/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC	C22B 5/00, 5/04, 5/12; C22C 1/04, 1/10; C04B 35/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8		
AU : as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT 9		
Category*	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
A	GB,A, 626653 (REGIE NATIONALE DES USINES RENAULT) 19 July 1949 (19.07.49)	(1 - 17)
A	FR,A, 856598 (GEUTSCHE GOLD-UND SILBER SCHEIDEANSTALT) 18 June 1940 (18.06.40)	(1 - 17)
A	FR,A, 1100993 (MEDVEDIEFF) 27 September 1955 (27.09.55)	(1 - 17)
A	US,A, 4668282 (GILMAN et al) 26 May 1987 (26.04.87)	(1 - 17)
P, A	WO,A, 89/10194 (SCIENTIFIC GENERICS LTD) 2 November 1989 (02.11.89)	(1 - 17)
(Continued)		
<p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
6 April 1990 (06.04.90)	18 April 1990	
International Searching Authority	Signature of Authorized Officer	
Australian Patent Office	B. BOURKE 	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	DERWENT ABSTRACT ACCESSION NO. 87-248251/35, Class L02, SU,A, 1281550 (VNIENERGOTSVEIMET) 7 January 1987 (07.01.87)	(1 - 17)
A	DERWENT ABSTRACT ACCESSION NO. 87-190393/27, Class P53, SU,A, 1169263 (AS SIBE MINERAL ORE) 23 November 1986 (23.11.86)	(1 - 17)
A	DE,A, 1261326 (DR.-ING. HELMUT v. ZEPPELIN) 15 February 1968 (15.02.68)	(1 - 17)

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 89/00550

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members			
US	4668282	AU	66601/86	BR	8700011
		EP	229499	JP	62146202
		PT	83942	ZA	8609425
				DK	6065/86
				NO	865063

END OF ANNEX